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CHARACTERISTICS OF OXYGEN ELECTRODES FOR LOW-TEMPERATURE FUEL CELLS

I. A. Denison

24 April 1961

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FOR THE COMMANDER:
Approved by

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ABSTRACT

Available information has been assembled and evaluated on the methods of preparation and the physical and electrochemical characteristics of oxygen for electrodes for low-temperature fuel cells. Porous carbon and sintered metal cathodes have been considered with reference to methods of preparation, mode of operation, electrochemical characteristics, and other properties. Such electrodes are capable of operation in strongly alkaline electrolytes at current densities of several hundred amperes per square foot for extended periods of time. Electrodes of noble metals, such as platinized platinum, are used in fuel cells in combination with an acidic or alkaline ion-exchange membrane electrolyte. Because of the slowness with which hydrogen peroxide is decomposed in acid media, fuel cells with acid electrolytes do not ordinarily operate at current densities greater than 20 amp/ft².

1. INTRODUCTION

The electrochemistry of the reduction of oxygen on active carbon surfaces has been described in detail by Yeager and coworkers (ref 1) and an extensive report dealing with the electrochemical reduction of oxygen on the surfaces of sintered metals is understood to be in preparation by Justi. However, details are not readily available concerning methods of preparation and performance of the various types of oxygen electrodes that have been designed and fabricated for use as the cathode elements of practical fuel cells. The purpose of the present report is to assemble significant information on the properties of oxygen electrodes that are contained in contractors' reports and other reports of limited distribution as a basic reference.

2. ELECTRODE POTENTIALS IN ACID AND IN ALKALINE MEDIA

The potentials of the reactions of the hydrogen and oxygen electrodes as given by Latimer (ref 2) are shown graphically in figure 1 as a function of the hydrogen-ion concentration of the solution. Potentials of the oxygen-peroxide electrode are also shown. The theoretical potential of the oxygen electrode for the reaction



is seen to be 1.229 v in a solution of unit hydrogen-ion activity (pH0). In a neutral solution (pH7), the potential of the oxygen electrode with reference to the standard hydrogen electrode is 0.815 v for the reaction



In an alkaline solution of pH 14, the potential of the oxygen electrode corresponding to reaction (1) is 0.401 v.

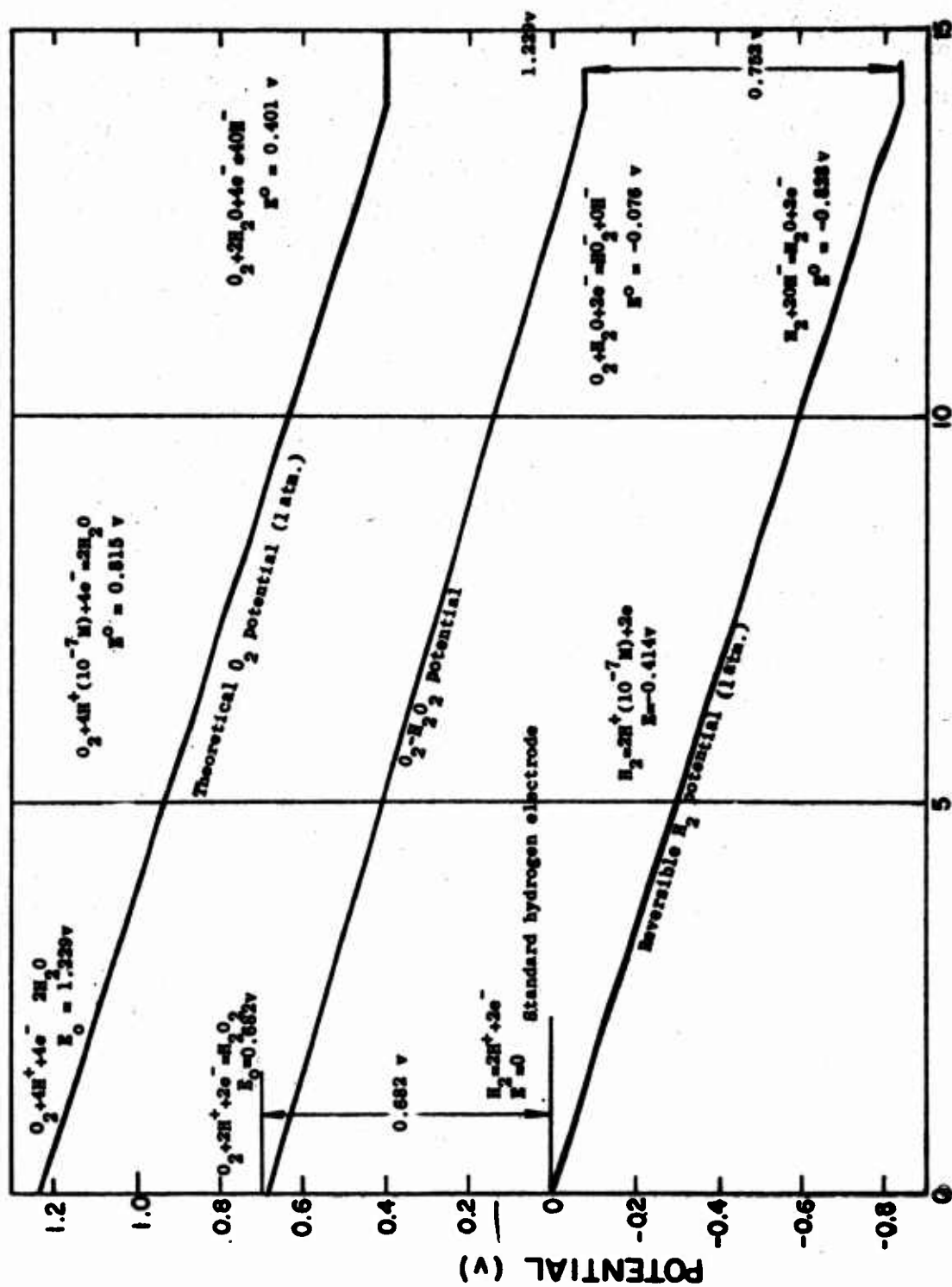


Figure 1. Potentials of the oxygen and hydrogen electrodes as a function of pH.

These theoretical potentials cannot be measured experimentally because the oxygen electrode is irreversible over the entire pH range. The potentials actually observed in alkaline solutions indicate that the oxygen electrode is reversible with respect to the peroxy ion (ref 1) according to the reaction



for which the standard potential is -0.076 v, according to Latimer.

Because of the low potential of the oxygen electrode at unit activity of hydroxyl ions (-0.076 v), the emf of a hydrogen-oxygen couple in an electrolyte at pH 14 is only 0.752 v (fig. 1). However, by incorporating a peroxide decomposing catalyst in an active carbon electrode, the concentration of peroxy ions on the surface of the electrode is greatly reduced by the reaction



with the result that the potential of the electrode approaches the theoretical potential of the oxygen electrode, namely 0.401 v. For example, for a concentration of 10^{-4} mole of hydrogen peroxide in 6N KOH, the calculated value of the potential of the carbon-oxygen cathode against a hydrogen electrode in the same solution is 0.903 v (ref 3). For a 10^{-10} molar concentration of peroxy ions, the calculated potential is 1.10 to 1.13 v (ref 4).

Since the oxygen produced by decomposition of peroxy ions according to reaction (4) is entirely reused by reaction (1), both atoms of oxygen in the oxygen molecule are utilized and the coulombic efficiency of the reduction of oxygen with the intermediate formation of hydrogen peroxide is identical with that of the four-electron process as given by reaction (1).

The theoretical and observed potentials of the carbon-oxygen electrode in strongly alkaline solutions are shown in figure 2, which is a reproduction of a figure prepared originally by Kordesch (ref 5). The potential of the catalyzed oxygen electrode against a hydrogen-carbon electrode in an approximately 50-percent KOH solution is seen to be 1.12 v, which corresponds to the open-circuit voltage of a modern hydrogen-oxygen fuel cell.

The potentials of the carbon-oxygen electrode shown in figure 2 apply to electrodes at atmospheric pressure. At partial pressures of oxygen less than 1 atmosphere, the observed potentials would be lower than the values shown in the figure. Kordesch and Martinola (ref 6) report a potential change of 0.038 v in 6N KOH for a 20-fold change in oxygen pressure. However, in less alkaline solutions, the electrode is apparently less sensitive to changes in oxygen pressure. According to Yeager (ref 1),

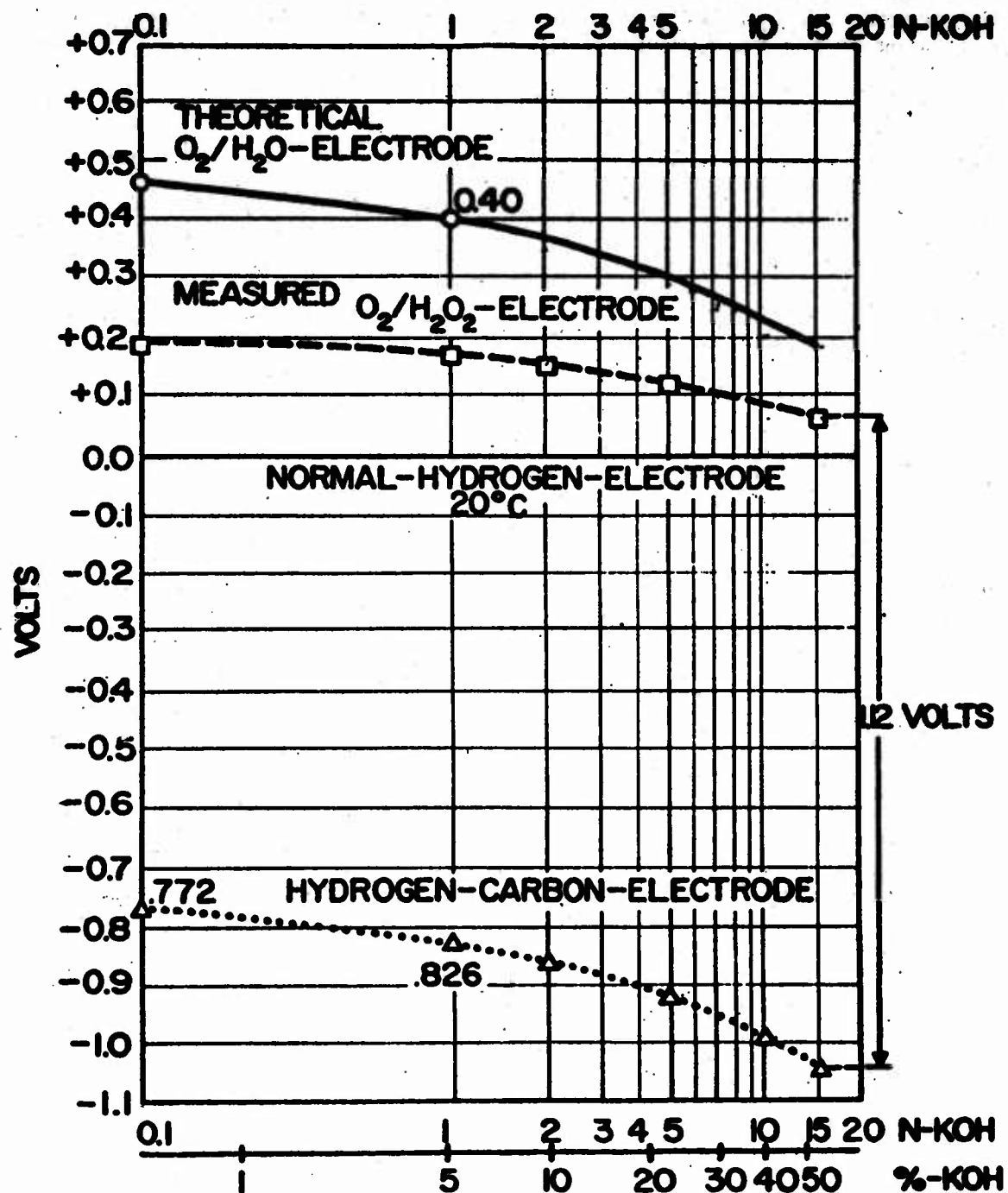


Figure 2. Potentials of hydrogen and oxygen electrodes in strongly alkaline solutions.

a 20-fold difference in the partial pressure of oxygen at pH values below 9 produces a change in potential of only 4 mv or less.

In considering the insensitivity of the oxygen electrode to change in oxygen pressure in acid solutions, Yeager (ref 1) raises the question whether oxygen may not be reduced in an acid medium by a mechanism that is entirely different from that which operates in an alkaline medium, citing the following mechanism suggested by Bratzler (ref 7) as follows:



where M is a reaction site. Nascent hydrogen produced by this reaction reacts with adsorbed oxygen to form hydrogen peroxide



According to Yeager, desorption of nascent hydrogen and reaction with oxygen, reaction (6), may be rapid compared with the rate at which hydrogen is produced by reaction (5). If so, increasing the oxygen concentration would be expected to have only a minor effect on the electrode potential.

Available evidence indicates that hydrogen peroxide is also an intermediate reaction product on oxide-covered surfaces of sintered metals, so that the measured potentials shown in figure 2 would be expected to apply to metal electrodes as well as to electrodes of porous carbon. With suitably catalyzed metallic electrodes contained in a hydrogen-oxygen fuel cell, Justi (ref 8) measured an open-circuit voltage of 1.12 v, which is identical with the difference in potential between the oxygen-peroxide electrode and the hydrogen-carbon electrode shown in figure 2.

3. POROUS CARBON ELECTRODES

3.1 Method of Preparation

Porous carbon cathodes have been used commercially for many years as a component of air-depolarized primary batteries in combination with a zinc-anode and an alkaline electrolyte (ref 9). These electrodes are required to operate only at moderate current densities, not exceeding 10 amp/ft², whereas some modern fuel cells operate at current densities as high as 300 amp/ft². The properties and performance characteristics of porous carbon cathodes developed to provide the high current requirements of the sodium amalgam-carbon/oxygen fuel cell are described in detail in a report of the National Carbon Company (ref 10). Except as noted in the text, the information contained in this section was taken from that report.

The carbon stock used in the preparation of the cathodes of the sodium amalgam-oxygen fuel cell was selected on the basis of its "activity." As defined in reference 10, the term activity covers a range of properties that fall into the following categories:

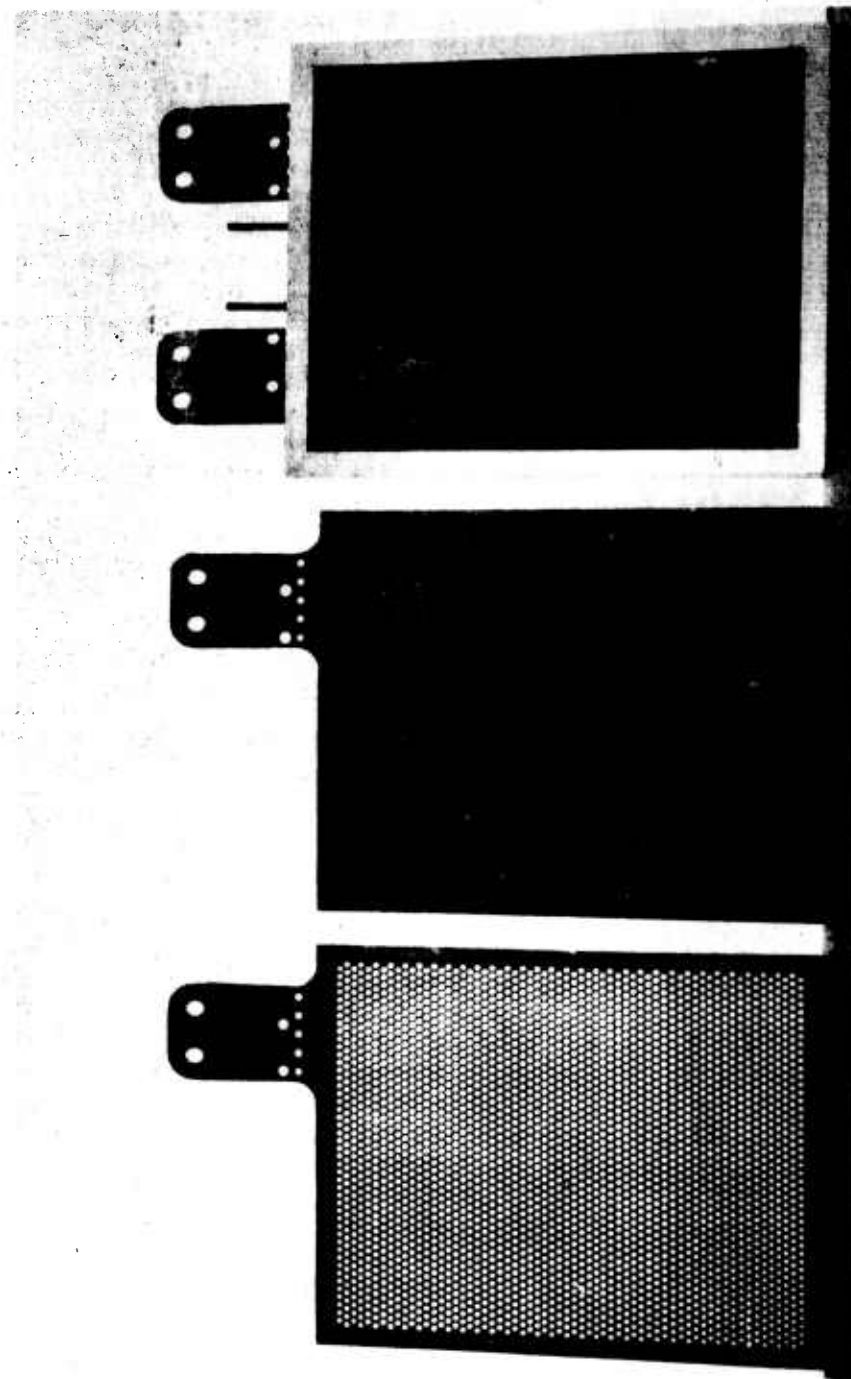
- (1) Surface development to provide a large electrochemically active area
- (2) Ability to decompose hydrogen peroxide
- (3) Formation of a network of interconnecting capillaries for rapid distribution of oxygen to the cathode-electrolyte interface.

Other essential characteristics of the active carbon are resistance to wetting and inertness toward the electrolyte. The activity level of the carbon stock was determined before and after electrode fabrication by measuring the time required to decompose hydrogen peroxide and by measuring polarization.

The following procedure was used for fabricating the oxygen cathodes for the sodium amalgam-oxygen battery. A 12-in. by 14-in. carbon panel, prepared by compressing activated carbon to a uniform thickness of 0.38 in. was cemented to a perforated steel backing plate 0.055 in. thick. The backing plate was provided with an unperforated edge and a tab extension for use as an electrical connector. Corrosion and oxide film formation on the backing plate was prevented by applying a chemically inert film of very low electrical resistance. For a double-faced cathode, two panels were assembled back to back in a precast plastic frame to provide an oxygen chamber. Figure 3, which illustrates the assembly of a double-faced cathode, was reproduced from the final report on the development of the sodium amalgam-oxygen battery (ref 10). Inlet and outlet tubes for oxygen are shown in the assembled electrode at the right in figure 3.

Development of process controls resulted in the production of active carbon electrodes that were sufficiently porous for high-rate discharge and that possessed inherent resistance to wetting without waterproofing. In fact, the depth of wetting in the electrodes during immersion in 5.5 M NaOH at 45°C for 1 year was only 1/32 in. Supplemental waterproofing was included, however, in the process of manufacture.

Silver metal in concentrations up to 15 percent of the weight of carbon was found to be an effective catalyst for the decomposition of hydrogen peroxide. Silver was incorporated into the carbon stock by treatment with silver nitrate which was converted to silver oxide by immersion in the alkaline electrolyte. Alternatively, silver nitrate contained in the porous carbon was reduced thermally to metallic silver. After fabrication, the surface of the electrode was impregnated with silver salts.



Perforated
backing plate

Carbon molded
on plate

Model of carbons
in plastic frame

Figure 3. Assembly of the cathode element of the sodium amalgam-oxygen battery.

3.2 Polarization

A typical polarization curve of a carbon-oxygen electrode with oxygen at atmospheric pressure is shown in figure 4. For current densities up to 300 amp/ft², no advantage was gained with an oxygen pressure greater than 18 to 20 in. of water. Although these data were taken in a 5N NaOH solution, they would be expected to apply to a KOH solution of the same concentration since Yeager has shown that the polarizing characteristics of a carbon-oxygen electrode in 5M solutions of KOH and NaOH are approximately the same (ref 1).

In view of Yeager's conclusion that activation polarization of the oxygen-peroxide couple on active carbon in alkaline solution is very small, the change in potential shown in figure 4 is to be ascribed to concentration polarization associated with the transport of oxygen through the electrode to the reaction zone and with the transport of reactants and products between the reaction zone and the bulk of the electrolyte. The linear portion of the curve at current densities greater than 50 amp/ft² indicates the presence of a resistive component at the higher current densities.

Current-potential curves made after a period of continuous discharge indicate that polarization tends to decrease for a period of time after which the potential stabilizes at a constant value. These effects are illustrated in figure 5, which indicates the polarization associated with the continuous discharge of a cathode at 100 amp/ft². Although data are shown for a period of 4 months only, it is understood that electrodes fabricated by improved techniques should operate continuously for 8 or 9 months at 100 amp/ft², and for more than 1 year at 50 amp/ft².

3.3 Resistance

The loss in potential of porous carbon cathodes produced by the IR drop through the cathode is indicated in figure 6 for two current densities, namely, 50 and 100 amp/ft². At the higher current density, the IR drop is seen to increase by a factor of two over a period of 6 months when it became equal in magnitude to the polarization at 100 amp/ft² indicated in figure 4.

One factor that would account for the increased resistance is the movement of the electrolyte into the carbon electrode. As the active interface progressed inward, the electrolyte conductance path lengthened, whereas the electronic conductance path correspondingly shortened. Since the conductance of the electrolyte was only one-third the conductance of the electrode, the net result was increased electrode resistance.

3.4 Life

For a given type of operation the life of a carbon cathode is determined by the time required for the electrolyte to penetrate the

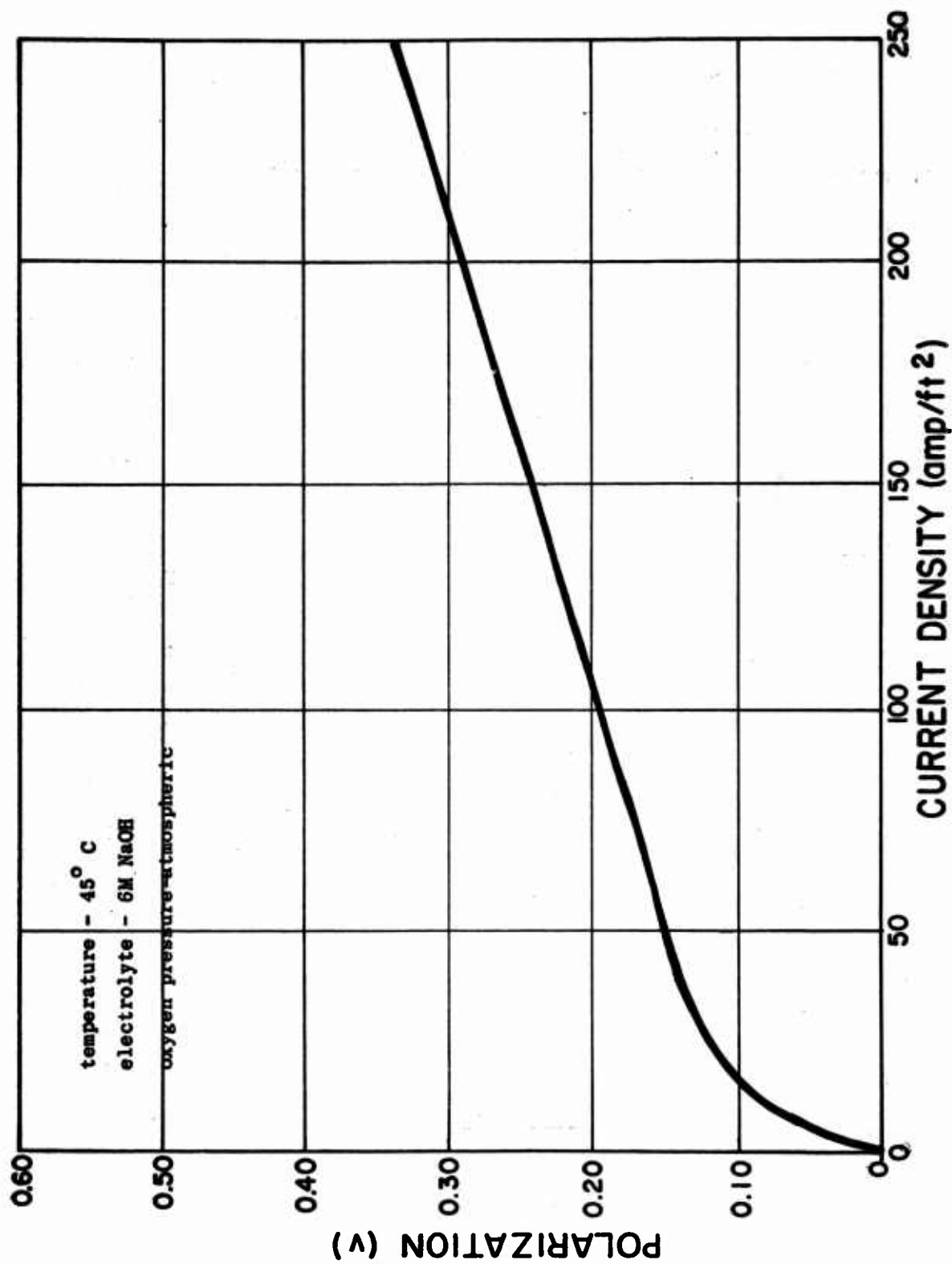


Figure 4. Polarization of the porous carbon cathode of the sodium amalgam-oxygen battery.

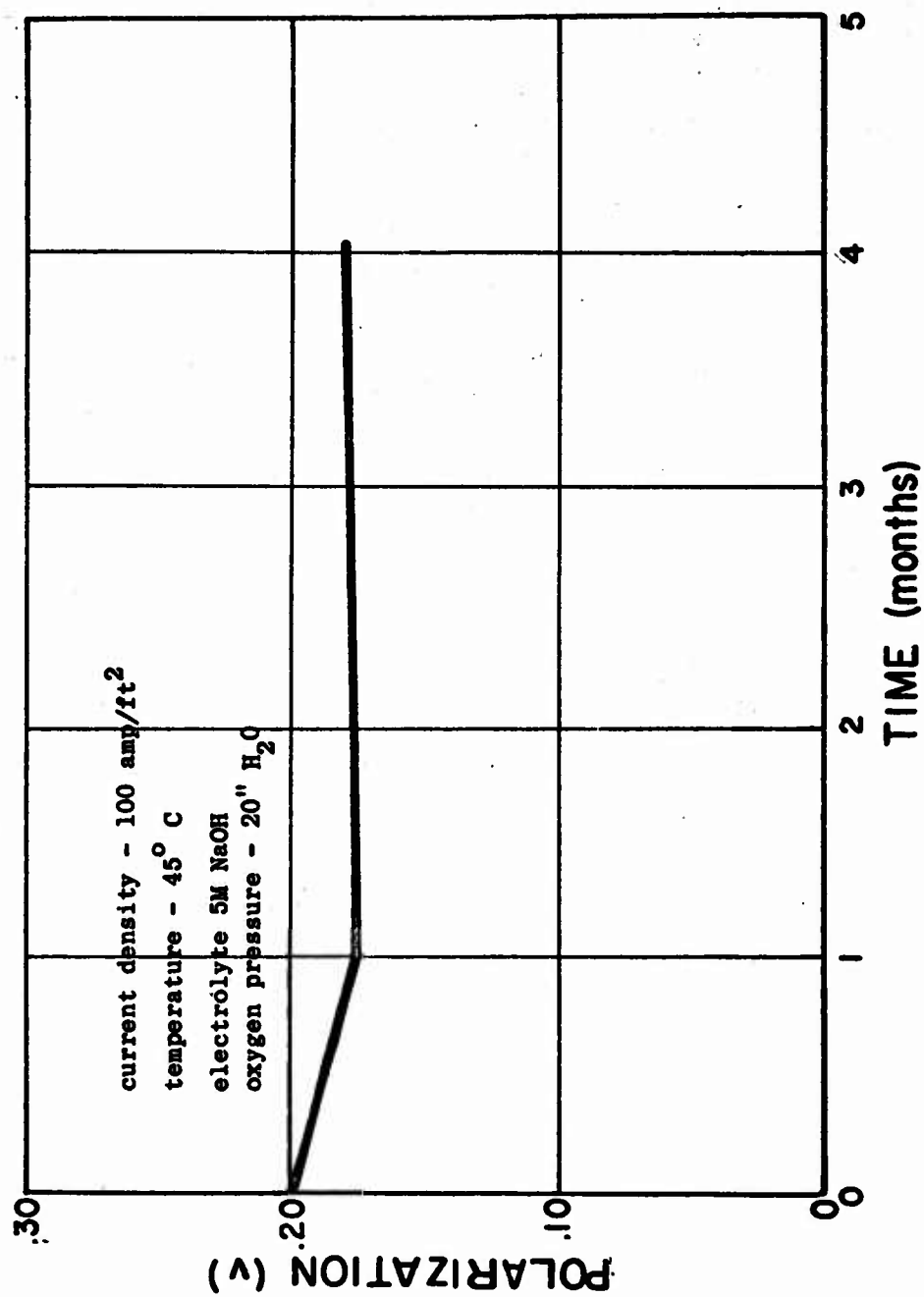


Figure 5. Polarization-time relation of the carbon cathode of the sodium amalgam-oxygen battery.

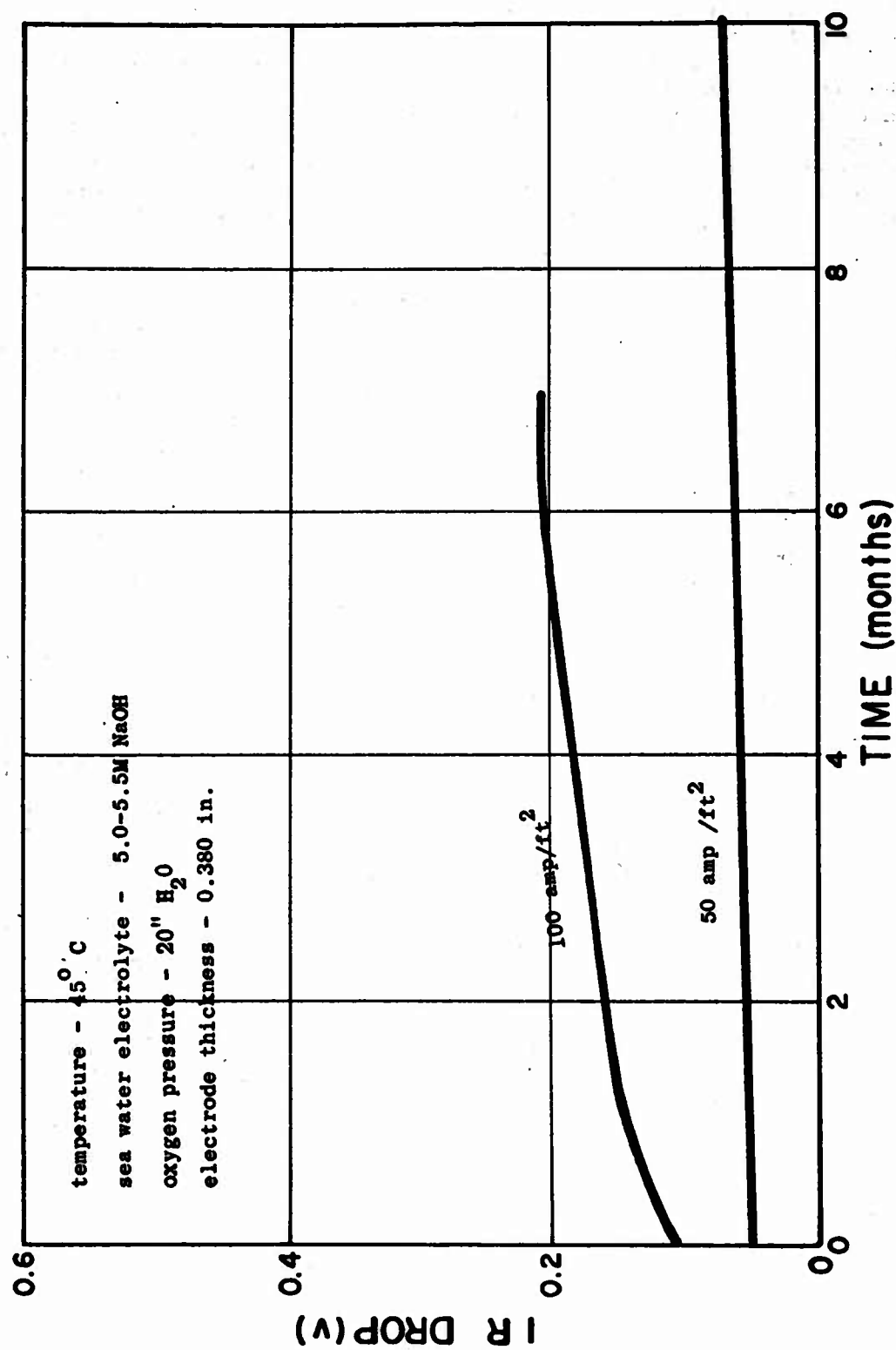


Figure 6. IR drop through porous carbon cathodes over extended periods of continuous discharge.

electrode from the solution side to the gas side. According to Yeager (ref 11), the static rate of penetration is accelerated by polarization, which produces chemical modifications of the reacting surface favorable to wetting. Hence, the higher the current density at which a cell is operated, the greater the polarization and the shorter the life of the cathode. A cathode discharged continuously at 50 amp/ft² operates for 1 year. Doubling this rate reduces the life by 20 to 30 percent. Intermittent overloads of 150 amp/ft² for 6 to 10 percent of the time do not impair performance at a normal load of 50 amp/ft². Overloads of 300 amp/ft² exceed the current density at which the electrode will operate normally.

Since the life of a carbon cathode is fixed by the time required for the electrode to be penetrated by the electrolyte, it follows that the thickness of the electrode can be adjusted to provide the desired period of operation. For example, for a period of continuous operation of 1 year at a current density of 50 amp/ft², calculation showed that a thickness of 0.38 in. would be required. For intermittent operation, the life of an electrode of this thickness would be proportionately extended.

3.5 Oxygen Utilization

The efficiency of utilization of oxygen was calculated by means of the expression

$$\text{Efficiency} = \frac{\text{No. of moles of } O_2 \text{ required for 100 percent efficiency}}{\text{No. of moles of } O_2 \text{ actually required}}$$

The number of equivalents of oxygen theoretically required to produce a given quantity of electricity is obtained, of course, from Faraday's law

$$Eq = \frac{it}{F}$$

where

Eq = number of equivalents of oxygen

i = current in amperes

t = time in seconds

F = 96,500 coulombs

The amounts of oxygen consumed in the operation of the test cell were measured by metering the oxygen entering and leaving the cell during discharge at different current densities. The amounts of oxygen corresponding to 100-percent efficiency were calculated from the cell current corresponding to each current density and the duration of

the discharge. In calculating the number of moles of oxygen actually consumed, it was assumed that hydrogen peroxide was decomposed completely and that utilization of all of the oxygen would require four electrons per mole of oxygen, and, therefore, an equivalent weight equal to one-fourth the molecular weight.

Average efficiencies calculated from data obtained with two types of cathodes gave values of 95 and 97 percent, the higher value being given by the more highly catalyzed cathode. Over the range of current densities used, with a maximum value of 175 amp/ft², the efficiency of utilization of oxygen was independent of current density.

In addition to the oxygen consumed electrochemically, additional amounts are required for operation of the cell, as for example, for purging the gas space behind each cathode. As oxygen is electrochemically consumed, any residue of inert gas, such as argon or nitrogen, however small in percentage with respect to the incoming oxygen, accumulates in the cathode chamber, thereby reducing the partial pressure of oxygen to the point where the amount of oxygen diffusing through the carbon to the reaction zone is insufficient to support the current. This condition is prevented in practice by purging the gas chambers behind each electrode continuously at a slow rate or by periodic rapid purges. According to Yeager (ref 11), the amount of oxygen required for purging may reach as high as 5 percent even though only 0.5 percent of argon is present in the oxygen.

3.6 Operation with Atmospheric Oxygen

The maximum current density that can be supported by carbon cathodes operating on air is limited by concentration polarization associated with the transport of air through the porous carbon electrode. This effect is illustrated in figure 7 in which are shown polarization curves of the oxygen-peroxide couple operating on air and on pure oxygen. These data, which were taken from a report by Yeager (ref 11), were obtained with active carbon electrodes containing no peroxide-decomposing catalyst in a 5N NaOH solution. The slight polarization indicated by curve B is in agreement with experience in showing that transport of oxygen is not a limiting factor in the performance of electrodes operating on pure oxygen.

According to Yeager (ref 11), a simple means of expediting the transport of atmospheric oxygen to the reaction zone is to reduce the thickness of the cathode element. This is implied in the following equation (ref 11)

$$i_L = \frac{\alpha \phi}{L} (P_{O_2}) \quad (7)$$

which relates the distance from the reaction zone to the rear surface of the electrode L (electrode thickness) to the limiting current density i_L for a given partial pressure of oxygen P_{O_2} at the rear surface of the electrode. In equation (7) ϕ is the pore cross section and α is a proportionality constant.

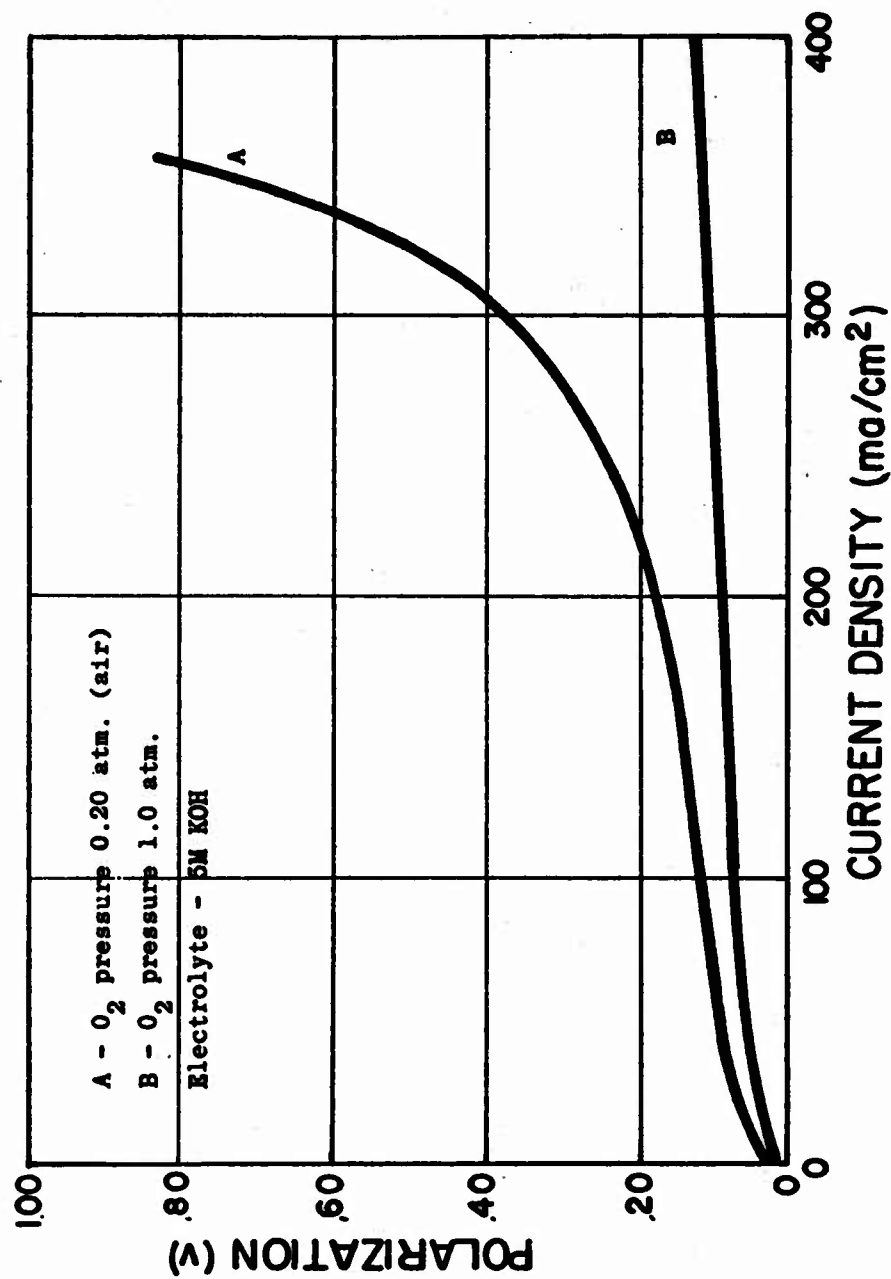


Figure 7. Effect of partial pressure of oxygen on the polarization of active carbon electrodes.

Reduction of the thickness of porous carbon cathodes to facilitate the transport of atmospheric oxygen has the disadvantage of curtailing operating life, which it will be recalled is determined by the time required for the electrolyte to penetrate to the rear side of the electrode. As shown in the next section, the life of sintered metal electrodes is not dependent on thickness, so that sintered electrodes need have only the thickness required for mechanical strength.

4. SINTERED METAL ELECTRODES

4.1 Method of Preparation

Sintered metal hydrogen and oxygen electrodes capable of sustaining high current densities at ordinary temperatures have been prepared by Justi and coworkers (ref 8) by combining the catalytic activity of Raney catalyst powder with the mechanical strength and good conductivity of sintered nickel. Raney alloy consists of a catalytically active component, usually nickel or silver, and a catalytically inactive component, which is either aluminum or zinc. The latter component is dissolved out of the mass, after pressing and sintering, producing the so-called double skeleton catalyst electrode (DSK). The preparation of the fuel electrode has been fully described by Justi (ref 8), but a detailed description of the oxygen electrode has not as yet been published. However, since the fuel oxygen electrodes differ only in the kind of catalyst used, the following description of the preparation of the hydrogen electrode may be considered to apply to the oxygen electrode also.

For the preparation of double skeleton electrodes, equal quantities of nickel and aluminum are first alloyed to form Raney nickel. After crushing in a ball mill, the powdered alloy is separated into fractions according to particle size. A definite fraction is selected and mixed thoroughly with nickel powder (prepared from nickel carbon) in some definite proportion, as for example, one part of Raney alloy to two parts of nickel. The powdered mixture is poured into a mold and compressed into a disk 4 cm in diameter and 2 to 4 mm thick with a pressure of about 4000 kg/cm². The disk is then sintered in an atmosphere of hydrogen for 30 min. at a temperature of 650° to 700° C. The aluminum contained in the Raney alloy is removed electrolytically by applying a positive potential to the electrode contained in a strong caustic solution.

4.2 Formation of a Stable Solution-Gas Interface

A sintered metal electrode prepared as described would not be suitable as a practical oxygen electrode in a fuel cell because the solution-gas interface would be unstable. Unlike a porous carbon electrode, in which the rate of penetration of the electrolyte is very slow, the sintered metal electrode would be quickly flooded with electrolyte unless

a positive pressure of gas were continuously maintained. However, a stable interface can be established by providing a finer pore structure in that part of the electrode which faces the electrolyte and a coarser pore structure in the other half.

The conditions under which a stable interface is formed in a complete sintered metal electrode have been represented graphically by Justi (ref 8) in figure 8. Layer 2 represents the single layer electrode prepared as previously described.

If the operating gas pressure \bar{p}_g is momentarily increased, the gas-liquid interface will tend to move into the finer pore structure of layer 1, where the surface tension is sufficient to accommodate the higher pressure. Conversely, if the gas pressure is momentarily reduced, the solution-gas interface will move into the coarser pore structure of layer 2.

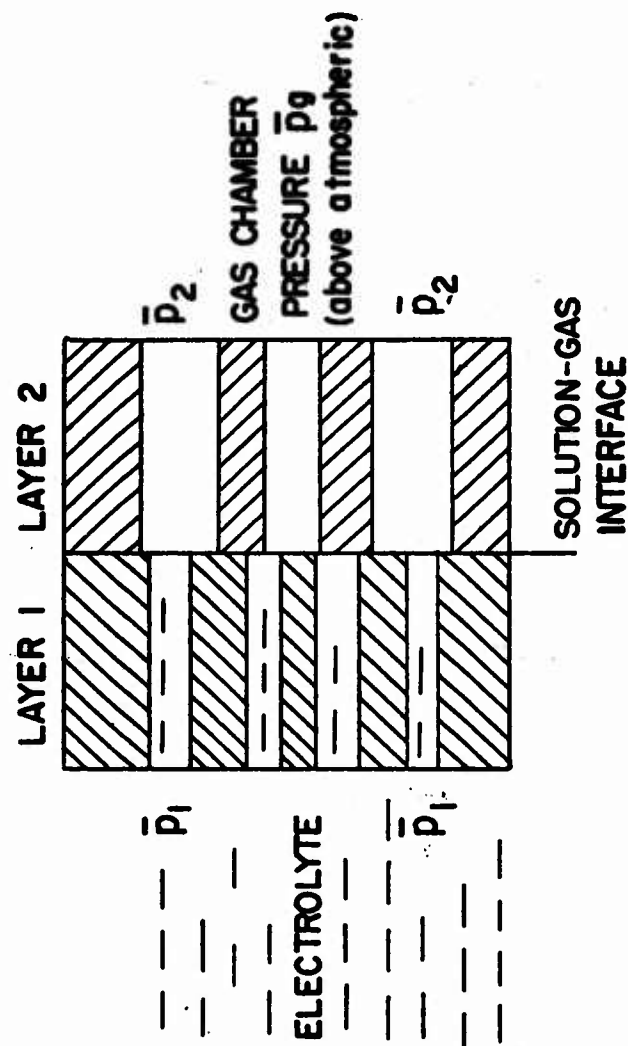
A double-layer DSK electrode is prepared by covering the mixture of powdered nickel and Raney alloy contained in a mold (layer 2) with a thin uniform layer of particles (layer 1) fine enough to provide a capillary pressure a few tenths of an atmosphere greater than the capillary pressure of layer 2.

Because double-layer sintered metal electrodes are not subject to progressive wetting, the life of sintered metal electrodes is obviously not limited by the time required for the electrolyte to penetrate completely through the electrode, as with active carbon electrodes. Hence, the thickness of a sintered electrode is determined only by the requirement of mechanical strength.

In the discussion of porous carbon electrodes (section 3.6), it was stated that oxygen transport is a limiting factor in the performance of porous carbon electrodes operating on atmospheric oxygen. As stated in section 3.6, a simple means of expediting the transfer of atmospheric oxygen to the reaction zone would be to make the electrode thinner. This suggestion, originally made by Yeager (ref 11), would not be applicable to porous carbon electrodes required to operate for long periods because reduction in thickness would curtail the operating life. However, full advantage could be taken of the suggestion by using sintered metal electrodes of minimum thickness consistent with adequate mechanical strength (ref 11).

4.3 Electrochemical Properties

In the preparation of the double skeleton oxygen electrode, Raney silver is used instead of Raney nickel (ref 8). The method of preparation and electrochemical characteristics of this electrode are understood to have been described in detail by Friese (ref 12). The potentials of the DSK hydrogen and oxygen electrodes are shown graphically in figure 9, which is a slightly modified version of a figure



\bar{p}_1 - average capillary pressure in pores of layer 1
 \bar{p}_2 - average capillary pressure in pores of layer 2
 \bar{p}_g - gas pressure
 Condition for a stable interface - $\bar{p}_1 > \bar{p}_g > \bar{p}_2$

Figure 8. Schematic cross section of a double layer DSK electrode.

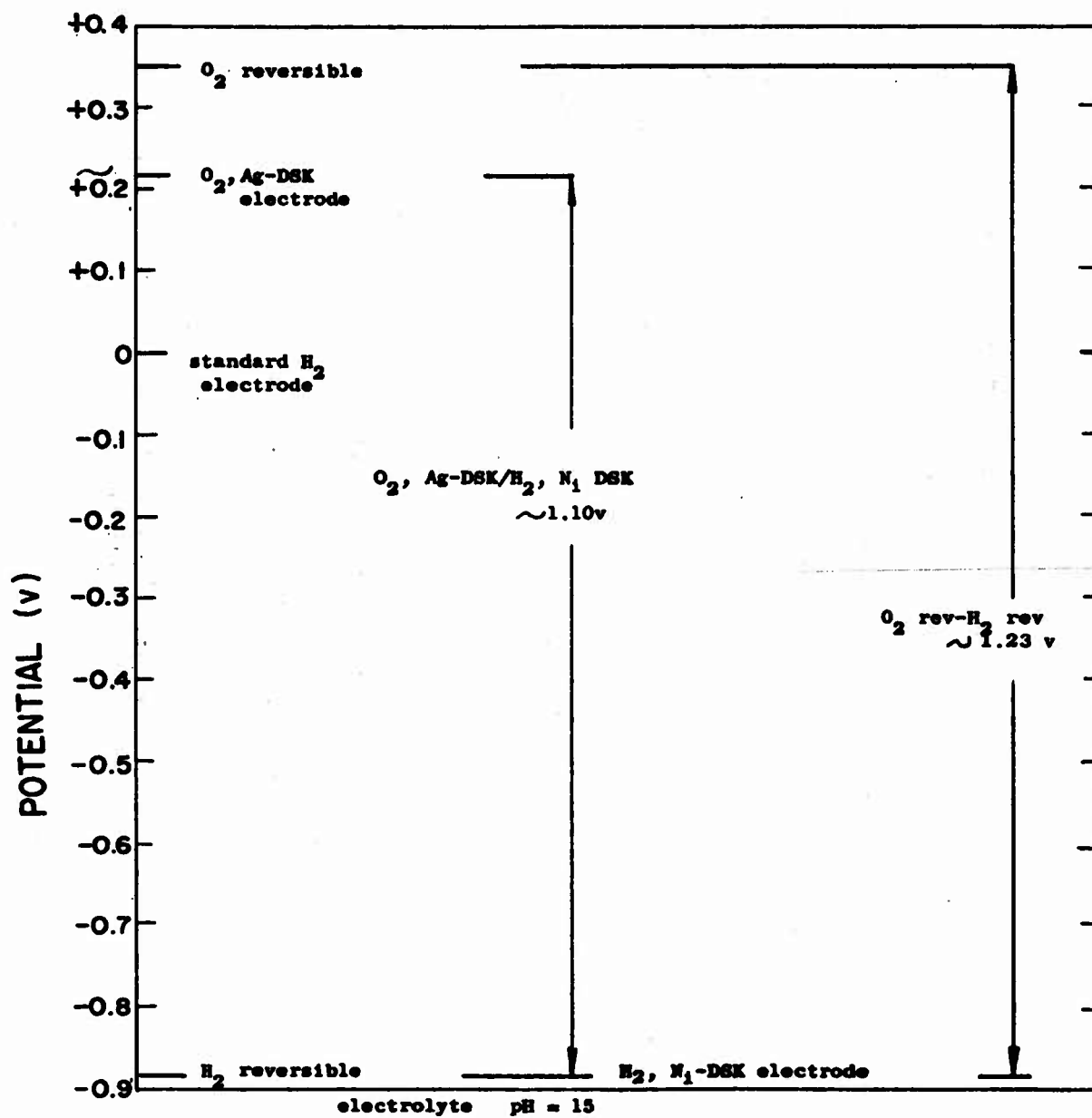


Figure 9. Potentials of the hydrogen and oxygen DSK electrodes.

prepared originally by Justi (ref 8). The current density-potential relation of the DSK oxygen electrode as reported by Justi is shown in figure 10. According to Justi (ref 13), a hydrogen-oxygen cell with DSK electrodes operated continuously for several months at the maximum current density indicated in figure 10, namely 500 amp/ft².

5. ELECTRODES WITH NOBLE METAL CATALYSTS

Noble metals, usually platinum or palladium, are used to catalyze the reduction of oxygen in the ion-exchange membrane fuel cell. In the original model of the cell described by Grubb and Niedrach (ref 14), the oxygen and hydrogen electrodes consisted of platinized metal gauze; but in a later modification of the cell, described by Cairns, Douglas, and Niedrach (ref 15), the catalyst layer was applied directly to the surface of the membrane electrolyte, the platinum gauze serving primarily as a current collector (type I cell). In the type II cell, in which the platinum gauze is eliminated, adequate conductivity and mechanical strength are provided by porous carbon disks that are pressed against the catalyst layer. The construction of the type I cell is illustrated in figure 11.

The electrolyte is a phenolsulfonic acid-formaldehyde ion-exchange resin. Hydrogen ions formed from gaseous hydrogen at the anode migrate through the electrolyte to the cathode, where they react with hydroxyl ions with the formation of water.

The open-circuit voltage of the cell is slightly more than 1 v compared with the theoretical value of 1.23 v, the deficiency of approximately 0.2 v indicating irreversibility at one or both electrodes. By means of an appropriate experiment, Grubb and Niedrach were able to show that the H₂/platinized gauze/H⁺ membrane half-cell operates at its reversible potential, thereby localizing the irreversibility of the cell at the oxygen electrode.

Potentials of the oxygen electrode of the ion-exchange membrane fuel cell made at different current densities and referred to a standard reference electrode have not been reported. All published polarization data are presented as cell-voltage-current density curves that include the total polarization of the anode and cathode and the IR drop within the cell as well.

The curves shown in figures 12 and 13, which were plotted from data reported by Cairns, Douglas, and Niedrach (ref 15), may be taken to represent the average performance of the type I cell. These data indicate that 20 ma/cm² is probably the maximum current density that can provide a useful voltage in acidic ion exchange membrane fuel cells in their present stage of development.

A recent application of the type I cell is the development of a regenerative unit in which the water formed during the operation of

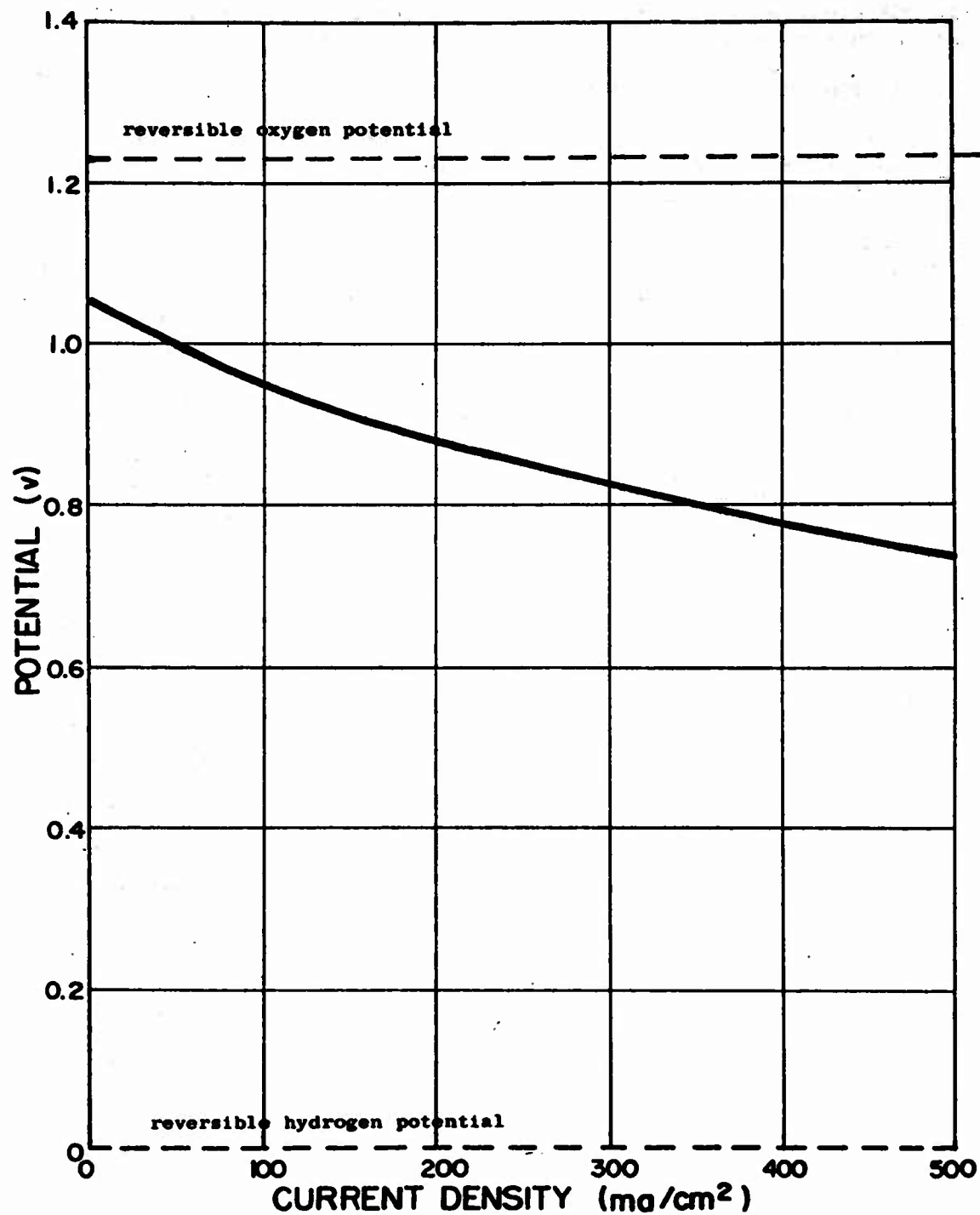


Figure 10. Current density potential curve of the Ag-DSK oxygen electrode at 85°C.

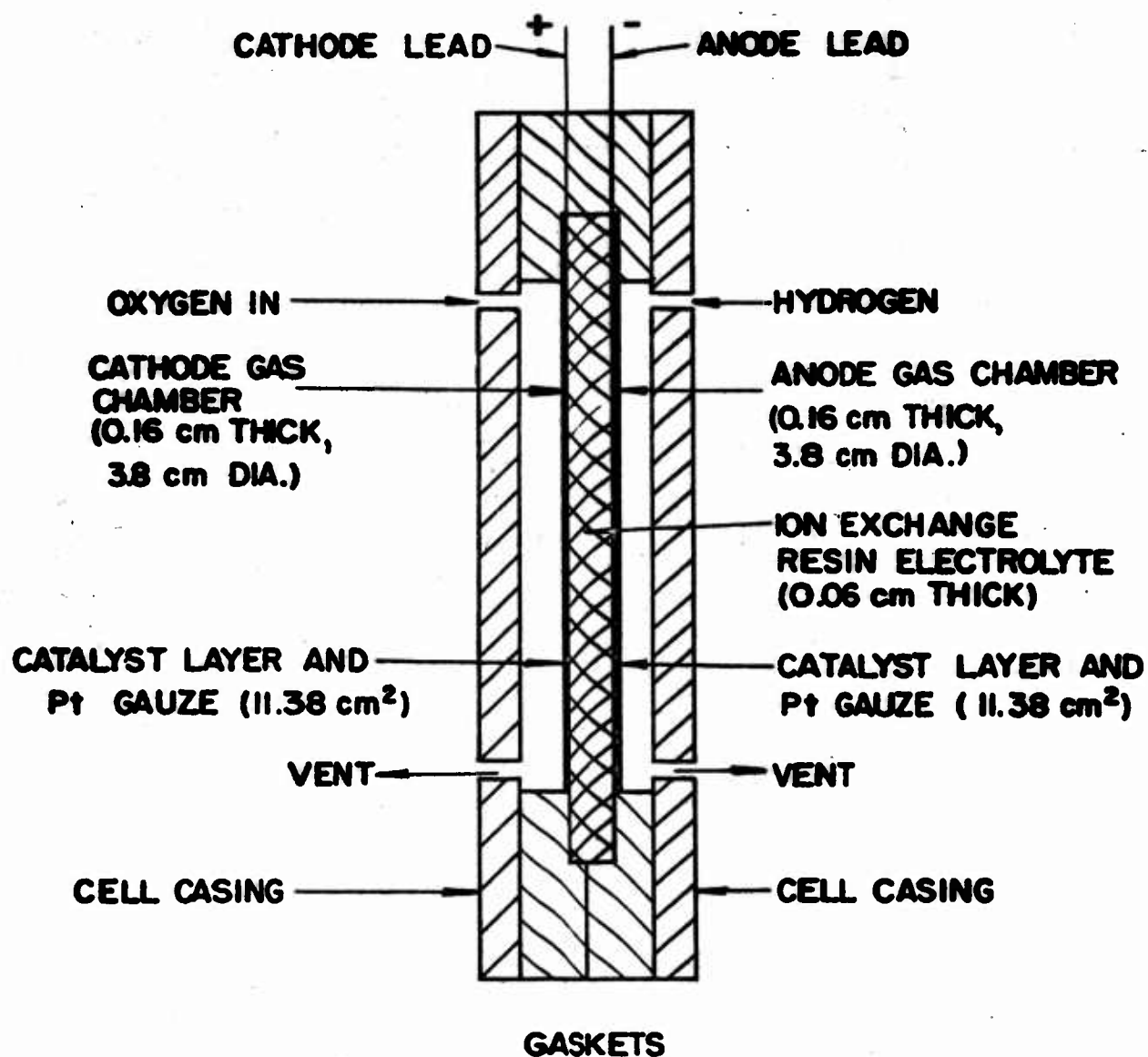


Figure 11. Structure of a type I ion-exchange membrane fuel cell.

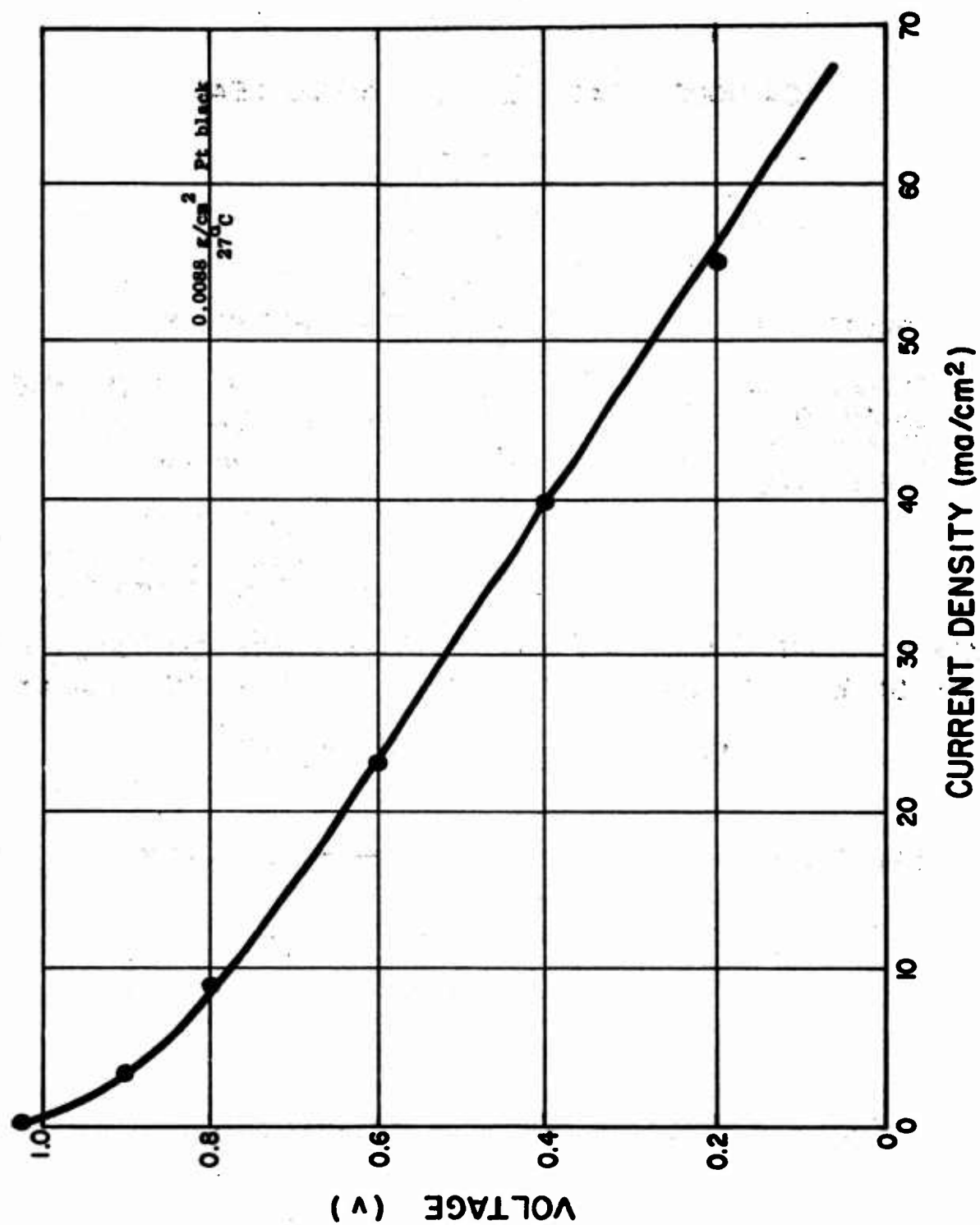


Figure 12. Current density-voltage curve of a type I fuel cell.

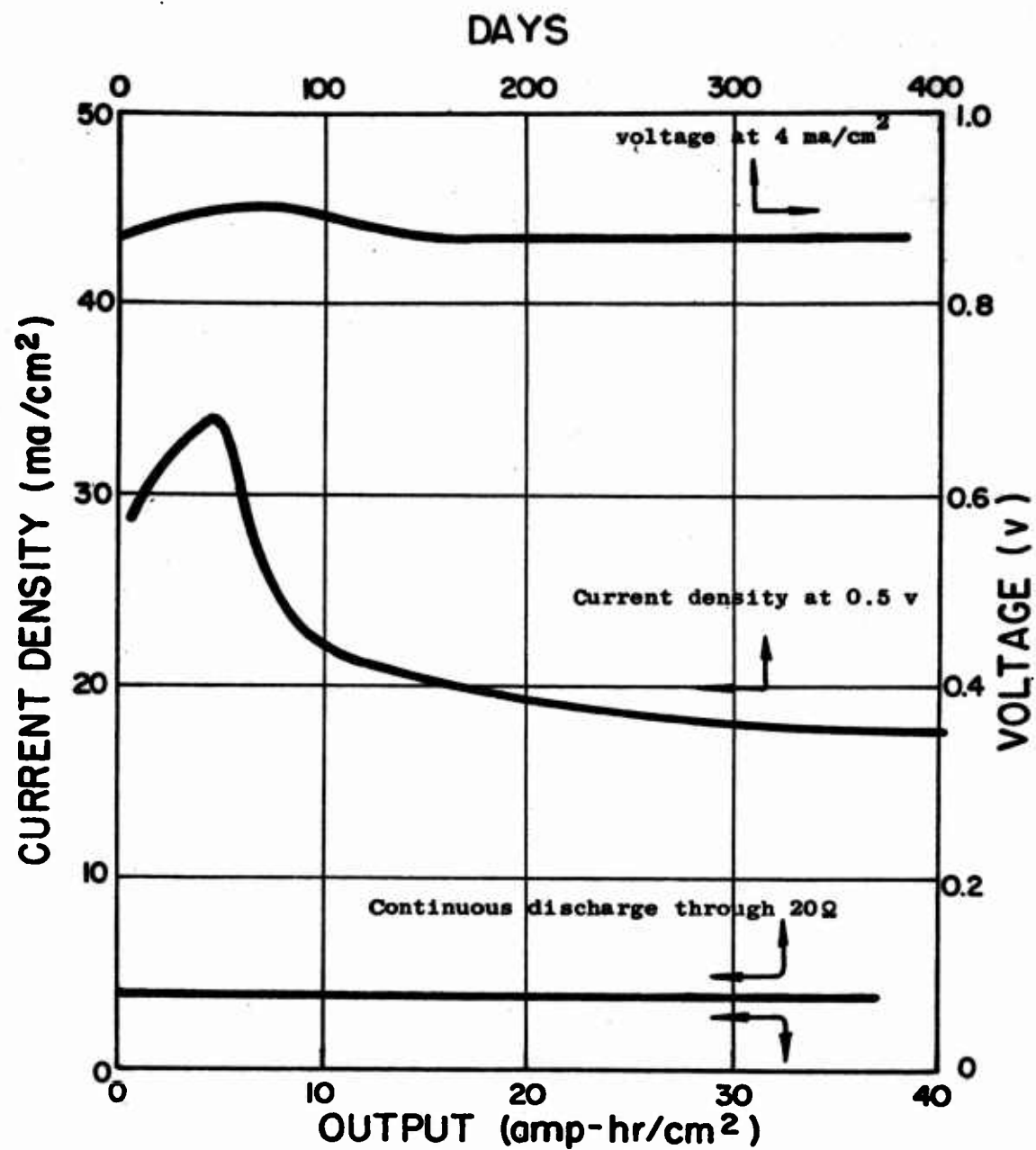


Figure 13. Discharge of type I cells through constant resistance and at constant voltage.

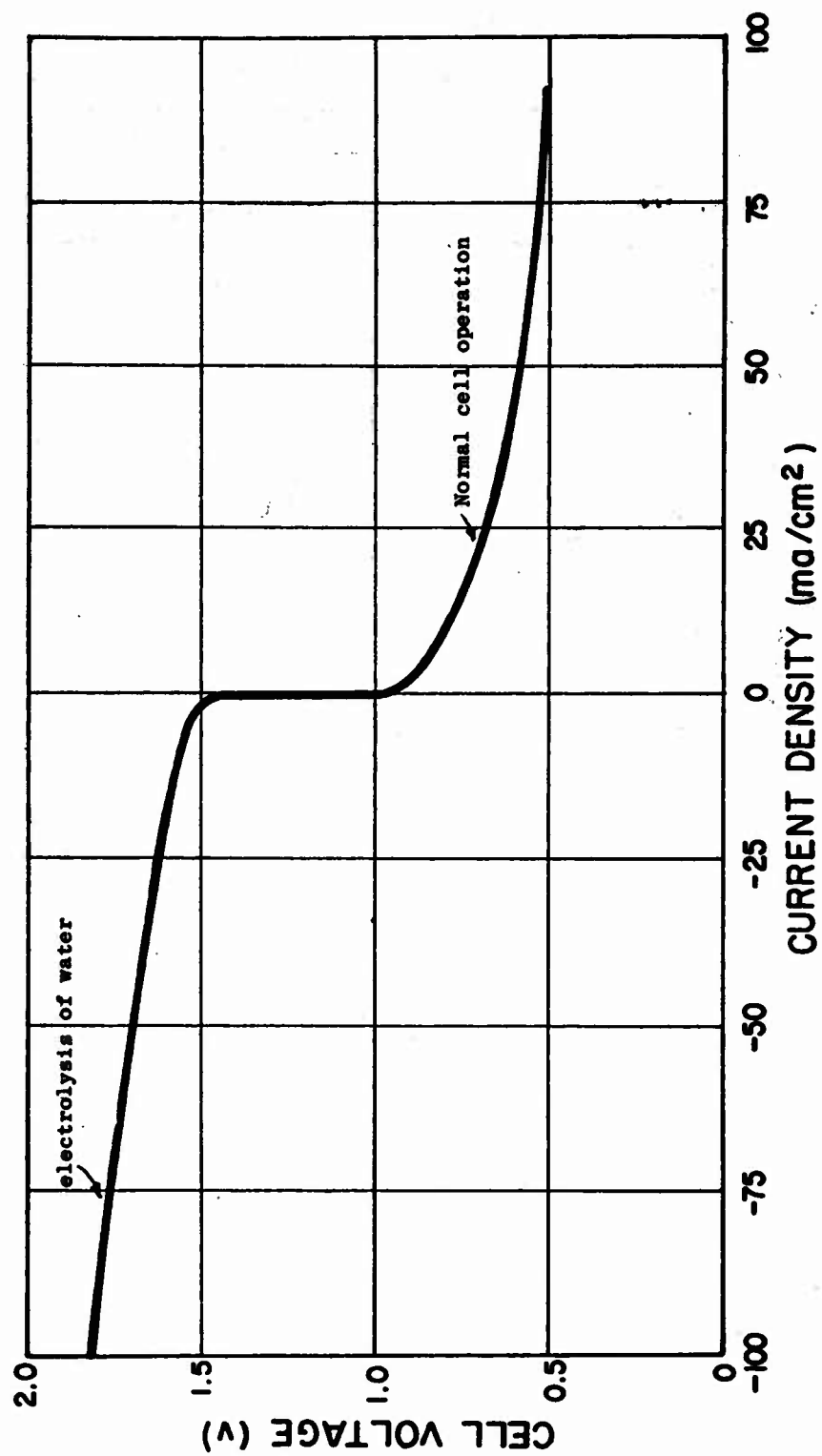


Figure 14. Current density-voltage curves for the charge and discharge reactions of an alkaline ion membrane fuel cell.

the fuel cell is electrolyzed for reuse as fuel and oxidant, respectively (ref 16). In the course of this development, it was observed that the reaction occurring during the charge part of the cycle increased the polarization of the oxygen electrode during the subsequent discharge because of desulfonation of the sulfonated phenol-formaldehyde resin and peeling of the catalyst from the gauze oxygen electrode. As one means of preventing this deterioration, the ion-exchange membrane was converted to the hydroxyl form and treated with a 30 percent KOH solution.

The performance of a type I cell modified by the substitution of an ion-exchange membrane in the hydroxyl form is shown in figure 14. This type of electrolyte is seen to provide a current density approximately as high as 80 ma/cm^2 at 0.5 v.

6. SUMMARY

It is intended that this report provide a summary of identifying characteristics and limitations of oxygen electrodes for low-temperature cells. The text represents selected information from the literature available as of January 1961. There are currently a number of government-sponsored and privately financed investigations which may contribute significantly to the capabilities of this electrode.

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